Art. II.—*The Spectra of Oxygen, Sulphur and Selenium, and their Atomic Weights.*

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The researches of Messrs. Runge and Paschen (Wiedemann's Annalen der Physik und Chemie für 1897, 8th Heft, pp. 641 and following) have revealed the existence of novel sets of spectra of great regularity, free from bands and differing, save for a few prominent lines, from the spectra of the same elements as observed by Pluecker, Hittorf and Huggins. The new spectra were obtained, when pure Oxygen or the acids of Sulphur and Selenium were heated in Geissler tubes to a temperature approaching 500°C. over a Bunsen burner while under the influence of an induction current and an air pump. Under these conditions the capillary part of the tube resolved itself into a pure line spectrum, while the wider parts showed a mixture of lines and faint bands. The line spectra of the three metalloids were arranged in triplets, forming two secondary series with indications of a primary series. With Selenium each triplet line seems to be sub-divided into two or more finer lines. The spectrum of Oxygen differed from those of Sulphur and Selenium by showing two additional secondary series of very close doublets with rudimentary members of a primary series.

Among the elements whose spectra have been arranged into distinct series Helium is the only one, which, like Oxygen, yields *two* separate sets of spectral series; and it may therefore be presumed that in both cases similar causes are bringing about the same results. Helium being regarded as a compound, consisting of Helium proper and Parhelium, which slightly differ in density, although no complete separation has yet been effected, it follows in reason that Oxygen must likewise be a compound.

To show that this conception does not clash with the investigations of the chemist, I beg to quote Debus (Liebig's Annalen der Chemie, 1888, Band 244, p. 144) who, after treating exhaustively on Ozone and its properties, says expressly: "The molecules of oxygen are by electricity broken up into atoms, which in statu nascendi unite with other oxygen molecules, forming ozone. The ozone molecules, by colliding with each other, are retransformed into oxygen molecules."

It would seem that, as the operations of Runge and Paschen were conducted at a temperature greatly exceeding the point above which ozone is able to exist (290°C.), a separation of the constituents of Oxygen takes place under the influence of heat and electricity.

From a consideration of the difference of the vibration numbers of the triplet and doublet lines, as given more fully later on, the atomic weight of the triplet constituent is 12, and of the doublet constituent 4. The former I propose to call Alphaoxygen, the latter Betaoxygen.

From a comparative table, furnished by the authors, it appears that six of the triplets of Alphaoxygen and five doublets of Betaoxygen coincide almost exactly with atmospheric lines. One triplet and two single lines, the latter of Betaoxygen, have also been observed among the bright lines of the sun's chromosphere. It would therefore appear that both gases are present in a free state either in the sun or in the earth's atmosphere, for the dark lines of the sun's spectrum, caused by Oxygen, would, after passing through a variable layer of terrestrial oxygen, be simply intensified, while the bright lines of the chromosphere would be correspondingly weakened. The preponderance of the dark over the bright lines observed would thus be accounted for. The presence of Alpha- and of Beta-oxygen in the sun may therefore be considered as fairly established.

The computation of the constants according to the formula, $\lambda_n = x + \frac{y}{n^2 - z}$ has been effected by means of the equations, published by the Royal Society of Victoria in their Proceedings for 1897, Vol. X. The equation of n may be simplified. If a, b, c, d, are the respective wave lengths of a sequence of four lines and $\alpha = \frac{(a-d)(b-c)}{(a-c)(b-d)}$, then $n = -1 \cdot 5 + \sqrt{\frac{\alpha}{4\alpha - 3}}$.

I may also call attention here to a few misprints occurring in the same paper. In the Table of Constants under x in the third column on the fifth line read 3421·05 instead of 2421·05, and on the last line 4081·66 instead of 4085·66.

While the computed and experimental values as a rule agree very closely, there are a few series, like the one of Betaoxygen, that cannot be brought into exact accordance. The reason of this peculiarity has yet to be accounted for.

The computation of the Constants in this paper has been done in the following manner. From the first four lines of each particular series I ascertained the value of root x. Comparing then the values of the normal series with the corresponding one of the abnormal series I selected the two that were in best accord. For Oxygen and Sulphur these happened to be the middle lines, for Selenium the least refrangible line. The difference of those two roots I found to be for Oxygen, ·0595, for Sulphur, 1·198, for Selenium, 1·063. Taking the mean of the two values for my corrected root, I determined the remaining three Constants from the first three lines. I then computed the wave numbers of the remaining lines of the series. Then, converting these wave numbers into their corresponding vibration numbers, I added or subtracted, as required, the mean difference of the vibration numbers of the triplets. This difference amounts to 3·70 and 2·08 in Oxygen, to 18·15 and 11·13 in Sulphur, and to 103·68 and 44·63 in Selenium. Having thus found the vibration numbers of the remaining series, I reconverted them into wave numbers and ascertained their Constants. The reader will find them in the accompanying Tables.

Of the doublet or Betaoxygen series Runge and Paschen have given the measurement of only one pair, viz., 6046·564 and 6046·336. Their respective vibration numbers are 16538·24 and 16538·94 or a difference of ·70. The mean root of the two subordinate series having been found equal to 4712·657 in wave numbers, their respective separate roots will be 4712·727 and 4712·587 with a difference of ·14.

Turning to the Table of Constants we find the difference of the roots of the first and third line of the triplets : Alphaoxygen = 1·072 ; Sulphur = 7·243 ; Selenium = 39·73. Taking the square roots of these numbers, we obtain Alphaoxygen = 1·04 ; Betaoxygen = ·37 ; Sulphur = 2·69 ; Selenium = 6·30.

TABLE OF WAVE LENGTHS I.

	ALPHA OXYGEN.						BETA OXYGEN.						SULPHUR.			
n+	*a*	R. & P.	*b*	R. & P.	*c*	R. & P.	*a*	R. & P.	*c*	R. & P.	*c*	R. & P.	*b*	R. & P.	*c*	R. & P.
1	7775·97	7775·97	9279·404		11303·62								13775·25		26233·74	
1	7774·30	7774·30	9276·194		11298·90		8846·12		11282·57		13170·71		13740·93		26109·42	
1	7772·26	7772·26	9274·432		11296·24								13719·94		26033·77	
2	3947·759	3947·759	6158·397	6158·415	6456·297	6456·287							7745·90		8714·90	
2	3947·661	3947·661	6156·993	6156·993	6454·756	6454·756	4368·466	4368·466	7002·48	7002·48	7254·32	7254·32	7735·02		8701·13	
2	3947·480	3947·480	6156·204	6156·198	6453·890	6453·900							7728·37		8692·71	
3	3339·552		5330·824	5330·835	5437·060	5437·041							6415·79	6415·68	6757·27	6757·40
3	3339·527		5329·774	5329·774	5435·968	5435·968	3692.586	3692·586	5958·75	5958·75	6046 564	6046·564	6408·32	6408·32	6749·06	6749·06
3	3339·463		5329·182	5329·162	5435·350	5435·371						6046·336	6403·76	6403·70	6744·00	6743·92
4	3112·756		4968·952	4968·94	5020·452	5020·31							5890·03	5890·08	6052·87	6052·97
4	3112·746		4968·040	4968·04	5019·520	5019·52	3443·74		5512·92	5512·92	5555·16	5555·16	5883·74	5883·74	6046·23	6046·23
4	3112·712		4967·526	4967·58	5019·008	5018·96							5879·89	5879·79	6042·16	6042·17
5			4773·913	4773·94	4803·230	4803·18							5614·58	5614·48	5706·48	5706·44
5			4773·070	4773·07	4802·375	4802·38			5275·10	5275·25	5299·09	5299·17	5608·87	5608·87	5700·58	5700·58
5			4772·598	4772·72	4801·897	4801·98							5605·37	5605·52	5696·97	5697·02
6			4655 595	4655·54	4673·938	4673·88							5449·94	5449·99	5507·31	5507·20
6			4654·688	4654·74	4673·127	4672·93			5131·49	5130·70	5146 59	5146·23	5444·55	5444·58	5501·81	5501·78
6			4654·343	4654 41	4672·675	4672·93							5441·25		5498·44	5498·38
7			4577·731	4577·84	4590·166	4590·07									5381·21	5381·19
7			4576·955	4576·97	4589·386	4589·16			5037·49	5037·34	5047·68	5047·88			5375·96	5375·98
7			4576·521		4588·947	4589·16									5372·75	5372·82
8			4523·731	4523·70											5295·91	5295·86
8			4522·975	4522·95					4972·34	4973·05	4979·59	4979·73			5290 84	5290·89
8			4522·519												5287·72	5287·88

The atomic weights of elementary bodies being directly proportionate to these numbers, as I have shown in regard to the Alkalies and Helium, and have also found to be true for other metals, we obtain the following atomic weights, when taking Sulphur = 32; viz., Alphaoxygen = 12·37; Betaoxygen = 4·40; Selenium = 74·91; or in round numbers: Alphaoxygen = 12; Betaoxygen = 4; Sulphur = 32; Selenium = 75.

The last number falls short by four of the atomic weight, found for that metalloid by chemists, but would seem to fit much better into the map of elements as arranged by Mendelejeff. Possibly Betaoxygen may enter into its constitution and thus complete its full atomic weight.

The principal series have been found to be represented by the head line and second line in Alphaoxygen, and by the second and third lines of Betaoxygen. Sulphur and Selenium have each only one line. Of the two last mentioned my formula can take no account; of the two first I have computed the probable Constants and a few additional members by availing myself of Rydberg's now well known law and assuming the most likely value for the modulus n. My results somewhat differ from the values computed by Runge and Paschen. Further, and, I hope not distant, observations may throw more light on the subject.